

MM 2: Battery Materials

Advanced Lithium-Ion Batteries

Time: Monday 10:15–11:30

Location: H 0106

MM 2.1 Mon 10:15 H 0106

A thermodynamic description of the battery material LiCoO₂ based on ionic and electronic work functions— •JOHANNA SCHEPP¹, STEPHAN SCHULD¹, RENE HAUSBRAND², MATHIAS FINGERLE², WOLFRAM JÄGERMANN², and KARL-MICHAEL WEITZEL¹ — ¹Philipps Universität Marburg, Chemistry Department — ²TU Darmstadt, Department of Material Science

The release of Li⁺ from stoichiometric LiCoO₂ (LCO) - a typical battery electrode material has been investigated by means of thermionic emission. Analysis of the data leads to an ionic work function of $w_{\text{Li}^+}(\text{LCO}) = 4.1$ eV. Combination of this value with the electronic work function $w_{\text{e}}(\text{LCO}) = 5.1$ eV also measured in this work by photoelectron spectroscopy, and information available from the literature allows to setup for the first time a complete thermodynamic cycle for a LiCoO₂ // Li battery. We arrive at an open circuit cell voltage of 2.4 eV in line with available literature information. The proof-of-principle study presented here provides experimental data on the binding energy values, i.e. chemical potentials, of Li⁺-ions and electrons and thus of Li-atoms in LiCoO₂ as battery cathode and is expected to open access to a better understanding and consequently also a better design of battery materials. Current efforts in measuring the long term characteristics of LCO as a function of the composition and the total amount charges exchanged will be discussed.

MM 2.2 Mon 10:30 H 0106

Effect of stress/strain on ionic and electronic conductivity in LiCoO₂ cathode material — •ASHKAN MORADABADI and PAYAM KAGHAZCHI — Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195, Berlin

It has been revealed that stress/strain can affect conductivity of materials up to several orders of magnitude [1]. In this study, we have investigated the influence of stress/strain on charge carrier mobilities in bulk LiCoO₂ using an ab initio-based “elastic dipole tensor” concept. It is shown that only 1% lateral tensile strain can increase the ionic conductivity in bulk LiCoO₂ more than two times [2]. The effect of longitudinal strain on ionic conductivity is even more significant [2]. Moreover, we calculated the electronic conductivity in bulk LiCoO₂ using hole-polaron hopping model. Our estimated value for the electronic conductivity is 2.7×10^{-4} S/cm [3] which is in good agreement with experiments ($1.0\text{--}3.3 \times 10^{-4}$ S/cm [4]). We find that the effect of stress/strain on ionic conductivity is stronger than that of the electronic one. By comparing the results obtained by this method and those calculated by DFT-NEB, we show that the “elastic dipole tensor” method can be used to estimate conductivity of materials under any given strain field with low computational and time effort.

[1] J. Garcia-Barriocanal *et al.*, Science, 2008, 321, 676-680. [2] A. Moradabadi *et al.*, submitted to Phys. Rev. Mats., 2017, arXiv: 1706.01709. [3] A. Moradabadi *et al.*, Phys. Rev. App., 2017, 7 (6), 064008. [4] Qiu *et al.*, Phys. Chem. Chem. Phys., 2012, 14, 2617-2630.

MM 2.3 Mon 10:45 H 0106

Pressure-dependence of the contact resistance in transport measurements of single secondary particles of Li(Ni_xCo_yMn_{1-x-y})O₂— •MARKUS S. FRIEDRICH¹, JANIS K. ECKHARDT¹, SIMON BURKHARDT^{1,2}, LIMEI CHEN^{1,2}, MATTHIAS T. ELM^{1,2,3}, and PETER J. KLAR^{1,2} — ¹Institute of Experimental Physics I, Heinrich-Buff-Ring 16, 35392 Gießen, Germany — ²Center for Materials Research (LaMa), Heinrich-Buff-Ring 16, 35392 Gießen, Germany — ³Institute of Physical Chemistry, Heinrich-Buff-Ring 17, 35392 Gießen, Germany

Lithium ion intercalating and deintercalating layered structured transition metal oxides, such as Li(Ni_xCo_yMn_{1-x-y})O₂ (NCM), are of interest for applications in lithium-ion batteries due to the predicted high capacity and the high cycling stability. Most studies on these

materials were carried out using composite electrodes which not only contained the active electrode material, but also additives that significantly influence the electrochemical properties of the electrode. A deeper understanding of the intrinsic properties of the active particles is needed, to examine the influence of the electrode-materials structure on energy storage and conversion of the cell system the material is used in. We developed a technique which allowed us to contact single particles of pure NCM with a controlled pressure and to perform electrochemical impedance spectroscopy to gain information about the electronic transport properties of the material. To contact the particles, they were arranged in trap holes, formed by photolithographical structuring of a photoresist, on top of a noble metal coated substrate.

MM 2.4 Mon 11:00 H 0106

Electrochemical Lithiation of crystalline Si investigated by operando NR and EIS— •ARNE RONNEBURG^{1,2}, MARCUS TRAPP¹, ROBERT CUBITT³, LUCA SILVI¹, SEBASTIAN RISSE¹, and MATTHIAS BALLAUFF^{1,2} — ¹Helmholtz-Zentrum Berlin, Institute of Soft Matter and Functional Materials, Hahn-Meitner Platz 1, 14109 Berlin, Germany — ²Humboldt-University Berlin, Institute of Physics, Zum Großen Windkanal 6, 12489 Berlin, Germany — ³Institute Laue Langevin (ILL), 71 avenue des Martyrs - CS 20156, 38042 Cedex 9 Grenoble, France

Silicon is a promising material for Li-Ion batteries due to its eleven times higher specific capacity compared to graphene. However, Si-anodes suffer from strong capacity fading. Therefore more fundamental understanding of the degradation is needed for further improvement. Neutron scattering is ideally suited for the investigation of the Li/Si system due to the high contrast between the scattering length densities. Si anodes were investigated with operando neutron reflectometry in parallel with electrochemical impedance spectroscopy to elucidate the solid electrolyte interface (SEI) layer growth and decomposition during (de-)lithiation. The lithiation kinetics were investigated over four cycles revealing a successive growth of the lithiated zone and the formation of a SEI-layer within delithiation and its decomposition during lithiation. The correlation of the integrated electric current with the Li fraction in the Si electrode discloses the amount of charge that is needed to dissolve the SEI-layer during lithiation. This necessary investment of charge is a reason for a low coulombic efficiency.

MM 2.5 Mon 11:15 H 0106

First-principles approach to lithium diffusion in silicon

— •VISHANK KUMAR, DAVIDE DI STEFANO, GIAN-MARCO RIGNANESE, and XAVIER GONZE — Institute for Condensed Matter and Nanosciences, European Theoretical Spectroscopy Facility, Université Catholique de Louvain, Chemin des étoiles 8, B-1348 Louvain-la-Neuve, Belgium

The high lithium storing capacity of silicon has drawn a strong interest for its possible application as an anode material in Li-ion batteries. However, the kinetics of lithium diffusion in silicon and in other lithiated phases of silicon, are not yet fully understood. In this study, the transition state theory was used to calculate the temperature dependent diffusion coefficient of Li, in bulk Si and LiSi phase. Quantum mechanical effects were also considered via semi-classical transition state theory. The energy barriers and pre-exponential factors have been obtained from total energy and phonon calculations, respectively, using the density functional theory (DFT). Kinetic Monte Carlo (KMC) simulations were used to calculate the effective diffusion coefficient in LiSi case with multiple vacancy mediated diffusion pathways.

Our results are in good agreement with the experimental data and suggest that quantum mechanical effects are only marginally significant in Li-Si system. The current study shows a theoretical approach, which is computationally efficient and quantitatively accurate, to fill the lack of studies on Li diffusion in lithiated Li_xSi phases.